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THE MOLECULAR STRUCTURE AND BEHAVIOR OF PHOSPHAZENES.(U)
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Calculations of barriers associated with crankshaft motions in polyphosphazenes were made. To properly handle polar bonds in conformational energy calculations a new method was worked out that removes difficulties previously associated with polarity. Parameters were worked out for alkyl halides and the method was tested on them and found to be successful. It was also applied to the polar polymers polyvinylchloride and polyvinylidenechloride. (cont. on back)		

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successfully. Dielectric measurements were made on poly bis(trifluoroethoxy) phosphazene and poly bis(p-methylphenoxy) phosphazene. Loss processes were identified with the side-group motions and glass transition in the amorphous fraction. The crystal disordering transition was accompanied by a large increase in conductance masking any dipolar loss.

THE MOLECULAR STRUCTURE AND
BEHAVIOR OF PHOSPHAZENES

FINAL REPORT

RICHARD H. BOYD

10 AUGUST 1977 - 9 FEBRUARY 1980

U. S. ARMY RESEARCH OFFICE

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TECHNICAL RESULTS

This project involved two thrust areas. One of them concerned the calculation of the conformational energetics of polyphosphazenes. The other concerned experimental measurements of the dielectric relaxation processes in polyphosphazenes.

1. Conformational Energetics.

Energy profiles were calculated for a variety of localized conformational transitions (crankshaft-like motions) in poly (dichlorophosphazene) and found to have low barriers. In extending these calculations to phosphazenes substituted with larger polar side-groups (OCH_2CF_3 , $\text{OCH}_2\text{C}_3\text{F}_8$, etc.) we decided that it was important to deal with a problem that has always existed in conformational energy calculations on polar compounds. That is, the problem of how to describe the electrostatic interaction energy between two polar bonds (dipoles) when they are separated by intervening atoms. The common expedient was to use a macroscopic dielectric constant in the electrostatic energy formulas. This clearly is only a crude approximation since the number of intervening atoms varies greatly with conformation and there is no assurance that the macroscopic approach is appropriate. We showed that it is perfectly feasible to handle the problem properly on a microscopic basis by means of polarization centers located in each bond. In applying the method to alkyl halides (as models where considerable test data exists) we found that

it worked well in simultaneously reproducing molecular polarizabilities, dipole moments (including strong inductive effects from substituents) and most importantly conformational energies.¹ At this point we felt that it was important to exploit and further test the approach by making calculations on well-known polar polymers containing halogens. We made calculations on the conformational energies of oligomers of polyvinylchloride (PVC). Experimental stereoisomer and conformer populations were satisfactorily reproduced. The oligomer energies were used to parameterize a statistical mechanical calculation of solution dimensions (characteristic ratio) and dipole moment for PVC. Good agreement with experiment was attained.² Calculations were also made on polyvinylidenechloride oligomers. Again, with a reasonable adjustment of the statistical weight parameters derived from the calculations good agreement with the experimental characteristic ratio and dipole moment ratio was attained.³ We believe the method developed is an important advance in conformational energy calculations and deserves further exploitation.

2. Dielectric Relaxation Processes in Polyphosphazenes.

Measurements of dielectric constant and loss were made over the range -196°C to 150°C and 10 Hz - 10 kHz on the crystalline polyphosphazenes $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ and $[\text{NP}(\text{O}\phi\text{OCH}_3)_2]_n$. A low temperature loss peak due to side-group reorientation

and a loss peak associated with the amorphous fraction glass-rubber relaxation were located and their activation parameters quantified.⁴ Our greatest interest was in studying the loss processes associated with the crystal transition in these polymers. We found that the transition in isochronal scans with increasing temperature was accompanied by a large increase in conductance. This conductance loss completely masks any dipolar loss mechanism. Experiments were conducted to manipulate the conductance loss. A high DC voltage was applied ("poling") in an attempt to sweep out ionic impurities. This did have the effect of reducing the conductance loss but it still remained high. The possibility exists that these materials (which have formal structures with conjugated backbones) are intrinsic semi-conductors.

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PERSONNEL SUPPORTED AND DEGREES AWARDED

Richard H. Boyd, principal investigator.

John Coburn, graduate research assistant, will be awarded
Ph.D. degree on thesis based in large part on
this work.

Laya Kesner, post-doctoral research associate.

Quang-Chung Yeh, graduate research assistant, awarded M.E.
degree.